Nanoparticle manufacture ambient air chemical and physical survey as a tool for accidental and chronic risk assessment

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Nowadays, nanotechnology lets foresee many opportunities and benefits for new materials with significantly improved properties as well as revolutionary applications in large industrial fields. Analysts have estimated that the size of the market was 900 million Euro in 2005 and will be 11 billion Euro in 2010.

However, nanomaterial industrial stakeholders are currently encountering potential problems with hazard control in their production plants. Release of nanoparticles in air can lead to violent chemical reactions and even explosions because of their small size and energetic properties, and hence high chemical reactivity.

Another major safety concern is the impact of manufacturing nanoparticles on the environment and more specifically on the health of workers and of neighbouring populations. Thus, a key issue consists of controlling the release of nanoparticles with chemical or physical toxicological impacts under the ambient background.

The methodology proposed here is based on ambient chemical and physical on-line characterisation. The LIBS technique has been proposed as an analytical technique for both on-line emission monitoring and workplace survey. As we also need on-line information on the particle size distribution, the DMA technique, which is based on electric mobility classification, has been combined to LIBS technique as shown by previous results on the DMA-LIBS combination (*Hahn and al, 000*).

The purpose of this work is then to optimise such a combination in order to reach ambient air characterisation of manufactured nanoparticles below 100 nm size.

Laboratory studies and optimisations are carried out in order to optimise the performance taking into account specific constraints for the development of a field instrument. As a consequence, increasing S R gain (ratio of the peak emission intensity over the average continuum emission) and therefore detection limit under a helium atmosphere (*Mukher ee and al, 005*) can not be applied in our case, as we have to deal with ambient air condition.

At a first stage, to valid the LIBS technique as a tool for chemical identification in ambient air, feasibility studies have been carried out on organic and non-organic trace element identification in bacteria (*E. coli*). The performance of the LIBS technique has been evaluated for several laser wavelengths (266, 532 and 1064 nm) and pulse durations (nanosecond and femtosecond) (*Baudelet and al, 005*). Our results show in particular the advantage related to the use of UV radiation (266 nm) for the detection of the metallic trace elements. The metallic element detection performance of the nanosecond UV laser is shown to be comparable to that of the ultra-short femtosecond laser, and to be much higher than that of nanosecond IR (or visible) laser as shown in the figure 1.

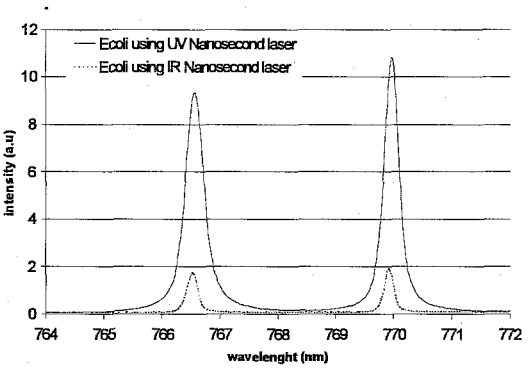

Figure 1: Comparison between potassium line emissions from bacteria (*E. coli*) excited by nanosecond UV or IR radiations at the same energy per pulse (the intensities of the K lines are normalized by the line intensity of the carbon 247.9 line).

In order to evaluate the feasibility of ambient air characterisation, a salt detection in ambient air using nanosecond IR laser pulses was carried out. A detection limit of 7 g m^3 with a S R of 1.2 was obtained for a size distribution centred at 50 nm. This performance fits well the criterion of risk assessment where a value smaller than 1 mg m^3 is required.

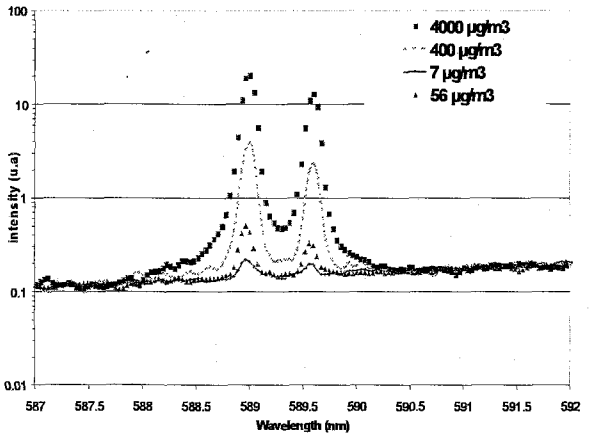

Figure. 2: LIBS detection of salt (the doublet of the Na) nanoparticles concentration in ambient air., The size distribution is centred around 50 nm for dry NaCl particles.

Based on these results, modifications on the optical setup are tested and laser studies are performed in order to decrease by a factor of thousand the detection limit of such preliminary results. In particular, S R gain studies have been performed using UV and IR nanosecond pulses but also evaluated the S R ration increase using femtosecond pulses. Tests currently performed were made on both nanoparticles of salt and metal in air matrix should permit to reach detection limit in ng m^3 range and thus in accordance with chronic risk assessment. Finally, we are performing new plasma laser generation to increase the S R gain by combining UV and IR nanosecond lasers in a dual pulse configuration.

CONCLUSIONS

It has been demonstrated the feasibility of an ambient air on-line characterisation of manufactured nanoparticles combining physical characterisation using dedicated DMA technique and chemical identification with field optimised LIBS technique. Results obtained on demonstrator based instrument should show detection limit around ng m^3 in UV-IR dual nanosecond pulse regime.

Keywords: *Nanoparticle, plasma, chemical analyses, size distribution, number concentration, on line*

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